Title	Non-linear rheological study of hydrogel sliding friction in water and concentrated hyaluronan solution
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Citation	Tribology International, 147, 106270 https://doi.org/10.1016/j.triboint.2020.106270
Issue Date	2020-07
Doc URL	http://hdl.handle.net/2115/84132
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Non-linear rheological study of hydrogel sliding friction in water and concentrated hyaluronan solution

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ABSTRACT: Studying sliding friction of hydrogels in liquid is important for understanding biological friction. This work applies the non-linear rheology approach to study the friction of elastic hydrogels against adhesive glass in water and in concentrated hyaluronan (HA) solution. Using a rheometer in parallel plate geometry, stress-strain Lissajous curves are obtained from the oscillatory strain sweep test. Non-linearity and energy dissipation are characterized the strain-hardening ratio S , and “energy dissipation occupancy” κ , respectively. For friction in water, a clear transition from a linear viscoelastic to non-linear viscoelastic response occurs at a critical strain amplitude. Whereas, in HA solution, significant friction reduction and non-linear viscoelastic response occurs, related to the rheological behaviors of HA film intercalated at the gel/glass interface.

KEYWORDS: friction of hydrogel, non-linear rheology, energy dissipation, Lissajous curve

1. Introduction

Friction occurs in the human body so smoothly that we do not notice, such as blood flow, joint motion, eyes blinking, and so on. The excellent friction reductions in biological systems are achieved by the soft and hydrated biological tissues and hydrated biopolymers as lubricants. For example, in knee joints, lubrication by synovial fluid that occupies the space between the articular cartilages decreases friction between them [1]. The articular cartilages are hydrogel-like materials while the main component of the synovial fluid is hyaluronan (HA), which is a polysaccharide. To understand the mechanism of the low friction of human knee joints, many researchers have reported on the friction and lubrication of poly(vinyl alcohol) (PVA) hydrogels [2-4]. Furthermore, in a previous study, we investigated the dynamic friction of hydrogels in HA solution as a model

system of articular cartilages [5] and confirmed the friction reduction effect of HA solution on the dynamic friction of PVA hydrogel sliding against a weakly adhesive glass substrate. The frictional stress decreases with an increase in the HA concentration at low sliding velocity, and the lowest friction appears in 10 c^* (c^* is the overlap concentration) HA solution; following that, it increases slightly with the concentration. By assuming that a continuous HA lubricant film is formed at the interface, which screens PVA adsorption to substrate, the thickness of the lubrication film in concentrated HA solution has been estimated [6].

In our previous studies, the hydrogel friction tests were performed on rheometers with parallel plates geometry in steady-state rotational motion [7,8]. The uni-directional rotational motion only reveals the dynamic frictional stress at steady-state, while the non-linearity and energy dissipation, which are two essential features for soft matter friction events, are not captured. In the present study, we intended to establish a novel rheological method to characterize these features. We adopted the oscillatory mode of the rheometer to measure the PVA hydrogel friction on hydrophobically treated hard glass substrate both in water and in concentrated HA solution. Such an oscillatory mode allows stress-strain Lissajous curves to be obtained at varied strain amplitudes [9]. From the Lissajous curves, the critical strain amplitudes to induce the rheological transition from linear to non-linear, which corresponds to the on-set of slide, were identified for the first time. Furthermore, energy dissipation before and after the linear to non-linear transition was analyzed.

2. Methods and materials

2.1. Hydrogel

Physically crosslinked PVA gels were used in this study, which were prepared by a quenching method from PVA solution of a solvent mixture (dimethyl sulfoxide: H₂O = 3: 1, w/w) [10]. The PVA solution of 10 wt% was prepared by heating PVA ($M_w = 90,000$, degree of polymerization = 2,000, degree of saponification = 99%, Nacalai Tesque, Inc.) in the solvent mixture for 1 hour at 90 °C. After heating, the degassed PVA solution was poured into a mold consisting of two glass plates (10 cm × 10 cm) with a silicone rubber spacer (3.0 mm) and this mold was quenched in a freezer at -40 °C for 16 h to form physically crosslinked gel. The mold was then warmed to room temperature and the gel sheet was removed and immersed in a large amount of pure water. Pure water was exchanged daily to extract the dimethyl sulfoxide in the gel sheet for one week. The equilibrium thickness of the gel in water was 2.4 mm. The modulus of the PVA gel was 54 kPa and was evaluated by compression test (see Section 2.4). Cylindrical gels with a 15-mm diameter were cut from the gel sheet for friction and mechanical measurements using a rheometer.

2.2. HA solution

The HA solutions were used as a lubricant for the frictional test. Solutions were prepared by mixing HA ($M_w = 2,000,000$, Kikkoman Biochemifa Co.), pure water, and 0.1-M sodium chloride for an inhibition of HA aggregation and 0.2 g/L sodium azide to suppress bacterial growth. The HA concentration of the solutions were 10, 20, 30, and 60 c*, where c* was the overlapping concentration which is defined as the point where the concentration within a given conformation's pervaded volume is equal to the solution concentration [11]; that of this HA was 0.28 g/L calculated by a formula in Mendichi et al. [12].

2.3. Friction substrate

We developed an *in situ* observation system for the frictional interface (as shown in the Supplementary Materials). We needed to use glass as a substrate for interfacial observation; however, because glass is hydrophilic, excess lubricant was present at the interface rather than the articular cartilage, and proper evaluation of the lubricant retention effect [13] by the HA solution was impossible. The use of a hydrophobic glass substrate in this system makes it easy to observe the interface contact because the lubricant is squeezed out from the interface of the hydrogel. A hydrophobically treated cover glass (Micro-cover glass C050701, Matsunami Glass Co., Ltd.) was used as the rigid counter substrate in the friction test. For the surface treatment, these glass pieces were firstly cleaned in an ozone cleaning chamber (UV/O₃). To prepare the hydrophobic surface, the cleaned glasses were exposed to a binding silane vapor, 1H, 1H, 2H, 2H, - Perfluorodecyltrichlorosilane (FDTS), at 20 kPa for 8 h in a vacuum desiccator. The contact angle to water of the treated glass was $110 \pm 2^\circ$.

2.4. Compression test

A compression test was performed with a universal mechanical test machine (Tensilon RTC-1310A, Orientec Co.). Cylindrical gel with a 15-mm diameter was compressed at a constant velocity of 0.2 mm/min to strain ~ 50%.

2.5. Rheological measurement

All rheological and frictional tests were performed on a strain-controlled rheometer (ARES-G2, TA Instrument Inc.) at 25 °C.

The viscosity of the concentrated HA solutions was measured with cone-plate geometry (diameter: 50 mm) with steady rotation mode. The shear rate $\dot{\gamma}$ varied from 10^{-3} to 10^3 s⁻¹. The

dynamic property of the HA solutions with 0.05 mm thickness was measured by the frequency sweep in the angular frequency range ω of 0.1 ~100 rad s⁻¹ at a shear strain of 0.5%.

The friction test of the PVA hydrogel was performed using disk-shaped gels. The center of the gel disk was aligned with the rotational axis of the rheometer. First, the bottom surface of the gel was bonded with a cyanoacrylate instant adhesive agent (Toagosei Co., Ltd.) to the lower plate of the rheometer, and then pure water or HA solution was poured on the top surface of the gel. Subsequently, the hydrophobic glass substrate fixed on the upper plate of the rheometer was allowed to approach from above the gel at a velocity of 2 $\mu\text{m/s}$, and then the upper plate was stopped when the normal pressure reached a preset value. A waiting time of 15 minutes was applied prior to the friction measurement, during which the normal pressure decreased slightly due to stress relaxation of the gel. To compensate for this change, the compression was adjusted slightly to maintain the preset normal pressure. The friction test was performed by applying rotational oscillation of the lower plate, which generates shear at the non-fixed gel/glass interface (see Figure 1).

Two experiments were performed. The first experiment was the conventional strain sweep mode of a rheometer. In this test, the gels were applied with a sinusoidal shear strain of $\gamma = \gamma_{\text{max}} \sin(\omega t)$ at an angular frequency $\omega = 1 \text{ rad s}^{-1}$ and a maximum strain $\gamma_{\text{max}} = 10^{-3}$ to 10^1 , and the torque $T(t)$ was measured. The γ_{max} is defined as $\gamma_{\text{max}} = R\theta/h$, where h (= 2.4 mm) and R (= 7.5 mm) are the gel thickness and the radius of the apparent contact area of the gel, respectively, θ is the maximum rotational angle and γ_{max} was varied by changing θ . The frictional force F was calculated from the torque as $F = 4T/3R$ [7]. The frictional stress σ was calculated as $\sigma = 4T/3\pi R^3$. The maximum oscillatory shear stress σ_{max} was obtained assuming a linear viscoelastic response of the measured

systems, $\sigma = \sigma_{\max} \sin(\omega t + \delta)$. Measurements were performed in pure water or in 30 c* HA solution with normal pressures of 11, 22, 33, and 44 kPa.

The second experiment was an oscillatory test to obtain stress-strain Lissajous curves. The gels were applied with an oscillatory sinusoidal shear of $\gamma = \gamma_{\max} \sin(\omega t)$ at an angular frequency $\omega = 1$ rad s⁻¹, at a specific strain $\gamma_{\max}$ for 20 cycles, and the stresses obtained in the 20th cycle were plotted against the shear strain (or shear rate). Measurements were performed in pure water or in 30 c* HA solution at a normal pressure of 33 kPa.

As control experiments, the strain sweep test and oscillatory test were also performed on the PVA gel with its top surface and bottom surface fixed to the upper and lower plates of the rheometer, respectively. Such tests on fixed gel without any slip reveal the bulk dynamic mechanical properties of the PVA gel. Hereafter, we refer to the gels with the bottom surface fixed and upper surface unfixed for friction text as slidable gels and the gel with two surfaces fixed as fixed gel.

3. Results

The HA solutions (10 c*~60 c*) showed typical rheological behaviors for concentrated polymer solutions, as shown in Figure 2. Shear thinning occurred in the high shear rate region (Fig. 2a), and the sol-gel transition occurred above some critical angular frequencies (Fig. 2b).

Figure 3 shows the log-log plot of maximum stress $\sigma_{\max}$ vs maximum strain $\gamma_{\max}$ curves measured by the strain sweep test for slidable gel in pure water and in the 30 c* HA solution. For comparison, the result for the fixed gel is also shown. In the case of the fixed gel, the stress-strain curve corresponds to the bulk deformation. A straight line with a slope of 1.0 was observed up to a large

strain (~ 0.5), and then a slight strain-hardening was observed at larger strains. For the slidable gels, the slope of stress-strain curves was also 1.0 in the small strain range both in water and in HA solution, as for the fixed gel. However, the stress-strain curves deviated from linearity and showed a strong strain softening at large strains. Specifically, in water, the critical strain amplitude for the deviation from linearity occurred at quite a large value ($\gamma_{\max,c} = 1$) and above this strain the stress started to decrease, while in HA solution, deviation from linearity occurred at a much smaller strain ($\gamma_{\max,c} = 5 \times 10^{-3}$). Furthermore, the stresses at the large strain region ($\gamma_{\max} = 2 \times 10^{-1}$) showed a peak in the HA solution, which differed from that in water. The stresses of the slidable gel in water were slightly lower than the fixed gel, almost independent of the normal pressure in the range of 11~44 kPa. On the other hand, in HA solution, the stresses were lower than those in water and increased as the normal pressure increased. These results indicate that HA solution forms a thin film at the gel/glass interface to reduce friction. A large normal pressure will squeeze out more of the HA solution to form a thinner film, therefore increasing the stress against the shear deformation. The deviation from the linearity suggests the slide of the gel under shear motion. Therefore, for the large strain range, $\gamma_{\max} > \gamma_{\max,c}$, the slidable gels should show a non-linear viscoelastic response, and the maximum oscillatory shear stress, $\sigma_{\max}$, (Fig. 3), estimated based on the assumption of a linear response, is no longer accurate.

To analyze the non-linear viscoelastic response and determine if the critical strain, $\gamma_{\max,c}$ observed in Fig. 3 corresponds to the transition from a linear to a non-linear response, we performed the oscillatory test and obtained the stress-strain Lissajous curves. A linear response gives a stress-strain Lissajous curve in an elliptical shape, while a non-linear response results in a distortion from the elliptical shape. Therefore, from the shape of the Lissajous curve, we can determine the critical strain for the transition from the linear response to the non-linear response with the increase of the

strain amplitude for each system. Furthermore, the behavior of energy dissipation can also be characterized from Lissajous curves.

As a typical example, Figure 4 shows the sinusoidal curves for stress, strain, and strain rate of the oscillatory test as a function of time (Fig. 4a), and the corresponding Lissajous curves (Figs. 4b and 4c) of the slidable gel in water around the transition strain $\gamma_{\max,c} = 1$. The strain rate curve was calculated from the strain curve by taking the derivative with respect to time, and the strain rate reached a maximum at strain 0. The stress curve showed a phase shift relative to the strain curve, and furthermore, the shape of the stress curve was distorted from the sinusoidal, indicating the non-linear viscoelastic response of the slidable gel around the transition strain. The stress-strain Lissajous curve rotated with time in a clockwise direction (Fig. 4b), while the stress-strain rate Lissajous curve rotated with time in a counter-clockwise direction (Fig. 4c). Slight distortion from the elliptical shape was also observed in these Lissajous curves.

Figure 5 shows the stress-strain Lissajous curves at varied maximum strain $\gamma_{\max}$ for different systems. From Fig. 5(a), the Lissajous curves of the HA solution showed good elliptical shapes, indicating that the HA solution was linearly viscoelastic over the observed strain range. On the other hand, from Fig. 5(b), the Lissajous curves of the fixed gel, which measures the deformation of the gel, were almost linear lines, showing no hysteresis loop. This result confirms that the gel is hyper-elastic with negligible energy dissipation during deformation. Figs. 5(c) and 5(d) show the Lissajous curves of slidable gel in water and in 30 c* HA solution, respectively. The Lissajous curves of slidable gel in water are approximately elliptical when $\gamma_{\max} < \gamma_{\max,c} = 1$ (Fig. 5[c-1]) and become distorted to parallel square shape when $\gamma_{\max} > \gamma_{\max,c}$ (Fig. 5[c-2]). This clearly confirms the interfacial slip of the slidable gel at $\gamma_{\max} > \gamma_{\max,c}$. It was surprising that large hysteresis loops

were observed, even in the region of $\gamma_{\max} < \gamma_{\max,c}$ where the Lissajous curves are in elliptical shapes, which is quite different from the behaviors of fixed gel that did not show hysteresis. This indicates that even in the small strain regime where the stress-strain curves obey linearity, the slidable gels already dissipate energy at the interface. In addition, it should be noticed that the maximum stress $\sigma_{\max}$ on Lissajous curves reached the highest value at $\gamma_{\max,c} = 1$ and decreased at larger $\gamma_{\max}$. This behavior is consistent with the results shown in Fig. 3. On the other hand, the Lissajous curves of the slidable gel in HA solution showed partially distorted elliptical shapes at very small strain $\gamma_{\max} = 0.001$, even below the critical strain $\gamma_{\max,c} = 0.005$ (Fig. 5[d-1]), and the distortion gradually increased with the strain until it reached a relatively large value (Fig. 5[d-2]). At a very large strain, the Lissajous curve also became a rectangular shape, indicating interfacial sliding, as also occurred in water. However, the sliding frictional stress in HA was one order of magnitude smaller than that in water. Such a friction reduction effect by HA solution at the interface is consistent with the result shown in Fig. 3.

To characterize the Lissajous curves from the viewpoint of non-linearity and energy dissipation, we used two dimensionless quantities; one was the strain hardening ratio, S , that characterizes the non-linearity of the Lissajous curves [14].

$$S = \frac{G'_L - G'_M}{G'_L} \quad (1)$$

As shown in Figure 6a, G'_L and G'_M are secant gradients at maximum strain and tangent gradients at zero strain on the Lissajous curves, respectively; G'_L and G'_M correspond to the elastic moduli in large and small deformation, respectively. An S value of 0 indicates a linear elastic response, a value > 0 indicates intracycle strain stiffening, and a value < 0 indicates intracycle strain softening.

The other is energy dissipation occupancy, κ , that characterize the relative energy dissipation in one cycle of the oscillatory test.

$$\kappa = \frac{E_d}{2\sigma_{max} \cdot 2\gamma_{max}} \quad (2)$$

Here, E_d is the energy dissipation density (J/m^3) for one cycle of the oscillatory test, which corresponds to the enclosed area of the stress-strain Lissajous curves, and the denominator $2\sigma_{max} \cdot 2\gamma_{max}$ in Equation 2 is the area of the rectangle circumscribing the Lissajous curve, as shown in Fig. 6b. For an elastic system, E_d is zero, while the E_d of a linear viscoelastic material scales to γ_{max} with an exponent of 2 [15,16]. As E_d depends on the moduli of the system, it prevents the comparison of the energy dissipation mechanism between different systems, while κ , the newly introduced parameter, enables the comparison of different systems. The κ takes values in the range of 0-1. For ideal elastic materials that show straight lines of Lissajous curves, κ is 0 because there is no energy dissipation. Whereas, for ideal viscous materials that have an elliptical shape of Lissajous curves, κ is $\pi/4 \approx 0.785$. For the linear viscoelastic material, κ has a value in the range of $0 < \kappa < 0.785$, whereas for a non-linear viscoelastic system, κ could be > 0.785 .

The strain γ_{max} dependences of S and κ for different systems are shown in Figs. 6c and 6d, respectively. For HA solution, S values were almost zero, however κ values were around 0.6 (i.e., lower than 0.785), indicating that the HA solution is a linear viscoelastic system in the strain range observed. For the fixed PVA gel, S was almost zero at the small strain regime but began to increase at a large strain regime, while the κ maintained a value of zero for the entire strain range. This confirms that the PVA gel is a hyper-elastic material, showing a linear response at a small strain, a non-linear response at a large strain, and negligible energy dissipation in the entire strain range.

For the slidable gel in water, S was almost zero at the small strain regime, however it increased abruptly when the strain $\gamma_{\max}$ exceeded the critical strains $\gamma_{\max,c} = 1.0$, indicating the transition from linear to non-linear responses. Surprisingly, κ values were around 0.5 even in the small strain ($\gamma_{\max} < \gamma_{\max,c}$), i.e., they were much higher than zero. This differed from the behaviors of the fixed gel. From the $S = 0$ and $\kappa > 0$, the response of the slidable gel in water was characteristic to a linear viscoelastic system at small strain. Furthermore, κ increased rapidly at large strain ($\gamma_{\max} > \gamma_{\max,c}$) and was across the red line for ideal viscous materials ($\kappa = 0.785$) and saturated to $\kappa = 0.9$. From the large S and κ , the slidable gel in water was strongly non-linear viscoelastic at a large strain, indicating the macroscopic sliding of the interface. These are shown in the videos in the Supplementary Materials. The bright area of the videos 1-3 shows a contact interface between the hydrogel and the glass substrate under applied shear strain in water. The increase of κ indicates that the sliding area was growing from the periphery of the hydrogel cylinder with increasing applied shear strain. The shear strain at which the hydrogel surface began to slide varied according to the distance from the rotation axis. It was clarified that the increase of the sliding area corresponded to the increase of the κ value. On the other hand, S and κ of the slidable gel in HA solution are very different from the behaviors of HA solution or slidable gel in water. The S of the slidable gel in the HA solution increased with $\gamma_{\max}$ even from a very small strain ($\gamma_{\max} = 0.001$), i.e., lower than the critical strain ($\gamma_{\max,c} = 0.005$), and reached very large values at large strains. On the other hand, κ increased gradually at $\gamma_{\max} > \gamma_{\max,c}$ and was across the red line ($\kappa = 0.785$) at around $\gamma_{\max} = 0.3$ and saturated to $\kappa = 0.9$. This result indicates that for the slidable gels in the HA solution, both non-linearity and energy dissipation increase gradually with the strain, and the transition from a linear to a non-linear response is not as sharp as that for the slidable gel in water.

4. Discussion

The results show that the slidable gel in water displayed linear viscoelastic behavior at $\gamma_{\max} < \gamma_{\max,c} = 1$ and a non-linear viscoelastic behavior at $\gamma_{\max} > \gamma_{\max,c}$. The latter corresponds to the slide of the interface. Therefore, what is the energy dissipation mechanism even prior to the occurrence of slide? For the slidable PVA gel in water, there was direct adsorption of the polymer strands on the surface of PVA gel to the hydrophobically treated glass substrate [17]. The dynamic adsorption-desorption provides a self-healing interface. With the absence of shearing deformation, the adsorption-desorption dynamics are in equilibrium and there is no energy dissipation. Under the oscillatory shear deformation, we observed the linear viscoelastic response when the oscillatory frequency was comparable to the adsorption-desorption dynamics. In the large strain regime in which the slide occurs, the frictional resistance of the gel comes from the elastic deformation of adsorbed polymer strands [18]. When the adsorbed polymer strands are detached from the substrate under shearing, the stored elastic energy of the strands is released and the energy is converted to heat, contributing to energy dissipation. The existence of a critical strain for the transition from linear response to the non-linear response indicates static-like friction behavior.

In HA solution, the HA film intercalated at the gel/glass interface screened the direct interaction of the PVA gel and substrate, which resulted in significant friction reduction. Accordingly, the non-linear viscoelastic behavior of the slidable gel in HA solution comes from the soft HA layer intercalated at the gel/glass interface. The rheology theory states that transient gel is formed when a concentrated polymer solution experiences a deformation with a strain rate faster than the inverse of the reptation time of the solution [11]. As shown in Fig. 2b, for the 30 c* HA solution used in this study, the angular frequency for the sol-gel transition was around 1 rad s⁻¹, above which the

solution behaved like a transient gel with a dynamic modulus in the order of 100 Pa. Since the modulus of the transient gel is much softer than that of the PVA gel (54 kPa), the shear deformation is mostly exerted on the HA layer and the true strain of the HA layer is much larger than the nominal strain, $\gamma_{\max}$, calculated from the thickness of the gel. Although the thickness of the HA layer is difficult to measure directly, a value in the range of 0.1~1 μm has been estimated from the frictional shear stress [6], which is 3-4 orders of magnitude lower than the bulk gel thickness (~ 1 mm) used to calculate the nominal strain $\gamma_{\max}$. Accordingly, the true strain on the HA layer could be 3-4 orders of magnitude higher than the nominal value shown in Fig. 3 and Fig. 5. Accordingly, the strain rate exerted on the HA layer is 3-4 orders higher than the nominal strain rate, $\dot{\gamma} = \omega\gamma_{\max}$. Even for the minimum strain tested ($\gamma_{\max} = 10^{-4}$) in this study, the true strain rate could be as high as 0.1~1 rad s^{-1} , which is close to the range of crossover angular frequency ($G' = G''$) for sol-gel transition (Fig. 2b). Such a high shear rate also induces shear thinning (Fig. 2a), and, therefore, the HA layer behaves as a transient physical gel to exhibit non-linear viscoelastic behavior even at a very small strain $\gamma_{\max}$. Above the critical strain ($\gamma_{\max,c} = 5 \times 10^{-3}$), the true strain becomes too high to rupture the transient gel. Therefore, the non-linear viscoelastic response of the slidable gel in HA solution is due to the dynamic rheological behaviors of the concentrated HA solution at the gel/glass interface.

5. Conclusions

Oscillatory shear test and stress-strain Lissajous curves are useful approaches to characterize the non-linear viscoelastic behaviors and energy dissipation of hydrogel friction. By using two dimensionless parameters (the strain hardening ratio, S , and the energy dissipation occupancy, κ),

the features of the Lissajous curves were well captured, which permitted us to systematically discuss the behaviors of the hydrogel friction in pure water and in concentrated HA solution with the increase of the strain amplitude $\gamma_{\max}$. The slidable gel in water showed a clear transition from a linear viscoelastic response to a non-linear viscoelastic response at a critical strain amplitude $\gamma_{\max,c}$, corresponding to the onset of macroscopic sliding. The energy dissipation at a small strain, even prior to the macroscopic sliding, indicated the dynamic effect of reversible bonds formed between the polymer chain and the substrate. The slidable gel in the HA solution showed remarkable friction reduction; however, the behavior is non-linear viscoelastic even at a very small $\gamma_{\max}$, and the non-linearity and energy dissipation both gradually increase with $\gamma_{\max}$. Such behavior is due to the non-linear rheological responses of the HA film intercalated at the gel/glass interface. The strain amplitude and strain rate exerted on the HA film were estimated to be 3-4 orders of magnitude higher than the nominal values to cause the non-linear viscoelastic response of the HA layer. The κ induced in this work is a convenient parameter that can be easily calculated regardless of the complexity of non-linearity. Thus, like $\tan\delta$ in dynamic viscoelastic measurements for linear properties, κ is a useful index to describe the viscoelastic properties of materials with non-linear responses.

Acknowledgements

This research was supported by JSPS KAKENHI Grant Numbers JP17H06144 and JP17H06376. Institute for Chemical Reaction Design and Discovery (ICReDD) was established by World Premier International Research Initiative (WPI), MEXT, Japan.

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FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4

FIGURE 5

FIGURE 6

FIGURE CAPTIONS

Figure 1. Schematic illustration of a set up for oscillatory frictional measurements between gel and glass. HA – hyaluronan.

Figure 2. Rheological properties of concentrated hyaluronan (HA) solutions at 25 °C. (a) shear rate dependence of viscosity, (b) angular frequency dependence of storage modulus G' and loss modulus G'' with shear strain of 0.5%. The crossover point between the G' curve and G'' curve determines the inverse of the reptation time of the solution in (b). The molecular weight of HA = 2,000,000.

Figure 3. Strain sweep results of poly (vinyl alcohol) (PVA) hydrogel friction in liquid, measured by applying an oscillatory shear $\gamma_{\max}\sin(\omega t)$ to slidable gel. The $\sigma_{\max}$ is the maximum oscillatory shear stress assuming a linear viscoelastic response of the system. The upper four curves show the results of oscillatory shear test in water, and lower four curves show those in 30 c* hyaluronan (HA) solution, under various normal pressures. Black closed circles show the strain sweep test of PVA gel bulk deformation using fixed PVA gel. Note that $\omega = 1 \text{ rad s}^{-1}$ was adopted.

Figure 4. (a) Sinusoidal curves of applied strain (middle), strain rate (lower), and the shear stress generated (upper) obtained by oscillatory strain test with slidable poly (vinyl alcohol) (PVA) gel in water (angular frequency $\omega = 1 \text{ rad s}^{-1}$, normal pressure 22 kPa). (b, c) The corresponding Lissajous curves of (b) strain-stress, and (c) strain rate-stress. One cycle of sinusoidal curves for stress, strain, and strain rate was divided into six sections and shown with three colors. The stress-strain Lissajous curve rotates with time in a clockwise direction (black arrows), while the stress-strain rate Lissajous curve rotates with time in a counter-clockwise direction (dotted arrows).

Figure 5. Lissajous curves of stress-strain for different systems. (a) Concentrated hyaluronan (HA) solution (30 c*), (b) fixed gel, (c) and (d) slidable gel in water and 30 c* HA solution, respectively, at a normal pressure of 33 kPa. The numbers in the figures are the applied maximum strains $\gamma_{\max}$. $\omega = 1 \text{ rad s}^{-1}$. The results in the 20th cycle are shown.

Figure 6. Characterization of non-linearity and energy dissipation of stress-strain Lissajous curves. (a) Definition of the strain hardening ratio S , which characterizes the degree of non-linearity of elasticity. (b) Definition of energy dissipation occupancy, κ , which characterizes the energy dissipation. The grey area enclosed by the stress-strain Lissajous curve stands for the energy dissipation density E_d for one cycle, and the red hatched area stands for $2\sigma_{\max} \cdot 2\gamma_{\max}$. (c, d) Oscillation strain dependence of S (c) and κ (d) against applied maximum strain $\gamma_{\max}$ for various systems estimated from Fig. 5. In (d), the red line indicates $\kappa = 0.785$ for ideal viscous materials and the black line indicates $\kappa = 0$ for ideal elastic materials. The result of silicone oil is shown as a standard for the pure viscous liquid.